[JP,2004-290748,A]

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FULL CONTENTS CLAIM + DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

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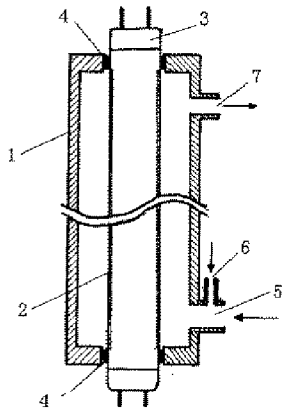
CLAIM + DETAILED DESCRIPTION

[Claim(s)]
[Claim 1]
A removing method of nitrogen oxides in gas which makes a photocatalyst which consists of fused silica which carried out halide acid treatment contact, nitric-acid-izes nitrogen oxides by a light response, irradiating a mixture of gas containing nitrogen oxides and oxygen with radiation, and is characterized by removing.
[Claim 2]
A removing method of nitrogen oxides in the gas according to claim 1 whose halide acid is hydrofluoric acid.

[Detailed Description of the Invention]
[0001]
[Field of the Invention]
This invention relates to the method of nitric-acid-izing nitrogen-oxides ******** NOx in the gas containing nitrogen oxides, such as polluted air, exhaust gas, and combustion gas, by a light response, and removing it.
[0002]
[Description of the Prior Art]
Since nitrogen oxides and what is called NOx have strong toxicity and it has become the leading role of environmental pollution, severe regulation is provided about diffusing in the air the gas which contains this in recent years, for example, the combustion gas from exhaust gas and plant of a car.
After [for this reason,] adding, the various methods, for example, the reducing hydrocarbon, for removing NOx in gas until now, How (refer to patent documents 1) to make a zeolite catalyst contact and to decrease nitrogen oxide, NOx is returned using the catalyst which consists of a rare earth metal, a transition metal, and noble metals, [by contacting the method (refer to patent documents 2) of using as molecule-like nitrogen, and the gas stream containing NOx into ozone and an oxygen mixture, oxidizing, and making N_2O_5 generate] The method (refer to patent documents 5) of carrying out plasma irradiation and carrying out reduction of the NOx, etc. are proposed contacting the method (refer to patent documents 3) of

Drawing selection
Drawing 1



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removing NOx, the method (refer to patent documents 4) of heating nitrogen oxides 2000K or more using thermal plasma, and decomposing, and exhaust gas containing NOx to activated carbon.
However, these methods do not escape becoming a cost overrun, in order to process a lot of gas, since a catalyst with a special presentation is used, or it is what needs special equipment.
[0003]
On the other hand, purifying the air or removing the nitrogen oxides in the air is also performed by irradiating with ultraviolet radiation under existence of a photocatalyst (refer to the patent documents 6, the patent documents 7, the patent documents 8, and patent documents 9).
However, most photocatalysts with which such a use is presented make titanium oxide a principal component.
Zinc oxide and cadmium oxide are only used slightly.

[0004]
In however, the charge site which these photocatalysts produced charge separation when the electron in a filled band was excited by the conduction band by the exposure of the near-ultraviolet light near 400 nm, and was carried out in this way and produced, A hydroxyl radical and a superoxide anion occur and an organic halogenated compound and an environmental pollutant like NOx are disassembled in these powerful oxidation operations.
However, the wavelength area where titanium oxide can demonstrate the photocatalyst ability is only near 400 nm, and there is a fault of not acting as a photocatalyst in the other wavelength area.
[0005]
[Patent documents 1]
JP,H6-31137,A (Claims, others)
[Patent documents 2]
JP,H8-238430,A (Claims, others)
[Patent documents 3]
JP,2002-119828,A (Claims, others)
[Patent documents 4]
JP,2002-273161,A (Claims, others)
[Patent documents 5]
JP,2001-314730,A (Claims, others)
[Patent documents 6]
JP,H8-7643,A (Claims, others)
[Patent documents 7]
JP,H4-307065,A (Claims, others)
[Patent documents 8]
JP,H4-307066,A (Claims, others)
[Patent documents 9]
JP,2001-25634,A (Claims, others)
[0006]
[Problem to be solved by the invention]
this invention -- acquisition -- it consisting of an easy material, and being effective in a large wavelength area, and, And it is made for the purpose of providing the method of nitric-acid-izing the nitrogen oxides in gas efficiently, and removing them, to nitrogen oxides using the new photocatalyst which has the nitric acid-ized capability by a remarkable high light response compared with titanium oxide, without needing a special device.
[0007]
[Means for solving problem]
The result of having repeated research wholeheartedly in order to develop a new photocatalyst effective in order that this invention persons may remove the nitrogen oxides in gas by a light response, The fused silica by which the surface was processed by hydrogen halide can nitric-acid-ize nitrogen oxides by a light response with the synchrotron orbital radiation of a also unexpectedly large wavelength area, And it finds out that a high nitric acid yield more remarkable than the titanium oxide system photocatalyst currently conventionally used most widely is shown, and came to make this invention based on this knowledge.
[0008]
That is, the removing method of the nitrogen oxides in the gas which this invention is contacted to the photocatalyst which consists of fused silica which carried out halide acid treatment, irradiating the mixture of gas containing nitrogen oxides and oxygen with radiation, nitric-acid-izes nitrogen oxides by a light

response, and is characterized by removing is provided.
[0009]
[Mode for carrying out the invention]
Although a photocatalyst used in this invention method is constituted as a subject, [a photocatalyst] [on substance] [fused silica which carried out halide acid treatment] This fused silica is transparent melting glass which carries out melting, solidifies under conditions strictly controlled so that impure part concentration was set to 50 ppm or less by using a source of a silicon oxide, for example, quartz, and quartz sand of natural origin as a raw material, and is obtained. This thing has the purity more than $SiO_2$99.995 mass %, and, [as non-purity] For example, less than aluminum:14ppm, As : 0.1 ppm or less, B:0.2 ppm or less, Ca: Less than 0.6ppm, less than Cd:0.01ppm, Cr : 0.05 ppm or less, Cu: Less than 0.05ppm, Fe : 0.5 ppm or less, K:0.6 ppm or less, Li: Less than 0.6ppm, less than Mg:0.1ppm, less than Mn:0.7ppm, less than Na:0.7ppm, less than nickel:0.1ppm, P:0.2 ppm or less, less than Sb:0.003ppm, less than Ti:500ppm, Zr: 0.8 ppm or less etc. are included. This thing shows strong absorption of OH kind in infrared-absorption-spectrum analysis.
Such fused silica is marketed from a general electric company (GE) as product name quartz watch GE124, 144, 214, 219, 224, 254, etc.
Although this fused silica is one sort of formless quartz glass, when the same formless quartz glass also uses synthetic quartz, it hardly shows the operation as a photocatalyst to nitrogen oxides.
[0010]
Next, halide acid treatment of this fused silica is performed by carrying out flush desiccation, for example, after fused silica is immersed in a halide acid aqueous solution. Under the present circumstances, as halide acid to be used, although there are hydrofluoric acid, hydrochloric acid, hydrobromic acid, etc., for example, especially hydrofluoric acid is preferred. these halide acid -- 1 - 50 mass % concentration -- it is preferably used as an aqueous solution of 5 - 20 mass % concentration. As long as the time which this halide acid treatment takes changes with the kind of halide acid to be used, and the concentration in that aqueous solution and a high-concentration aqueous solution is generally used for it, a short time may be sufficient as it, if a low-concentration aqueous solution is used, it will require a long time, but it is usually chosen in the range for 5 to 60 minutes.
[0011]
Thus, the photocatalyst of this invention obtained is a dense solid after density ^{3} of 2.2-2.3g/cm, and tabular, grain form, powder, the shape of a block, fibrous, etc. can make the shape form arbitrarily according to a request.
[0012]
Although the photocatalyst of this invention has the operation which disassembles nitrogen oxides by the exposure of radiation, [a photocatalyst] As these nitrogen oxides, the nitrogen oxides leading to air pollution, such as zinc-ized nitrogen N_2O, the nitrogen monoxide NO, nickel sesquioxide N_2O_3, and nitrogen dioxide NO_2, can be mentioned.
[0013]
Oxygen is mixed to nitrogen oxides, and a predetermined photocatalyst is made to contact, in order to nitric-acid-ize nitrogen oxides by a light response and to detoxicate them using a photocatalyst in this invention method, irradiating this mixture with synchrotron orbital radiation.
Although a semiconductor photocatalyst like old TiO_2 or ZnO shows the decomposition capability, [a semiconductor photocatalyst] [only in the optical absorption field of nitrogen oxides] In [in the light of the other wavelength, in order not to demonstrate catalyst capability, when natural light like sunlight is used, do not escape that the utilization efficiency of light becomes low, but] this invention method, Since a photocatalyst can disassemble nitrogen oxides also by the light of the wavelength which hardly shows optical absorption, there is an advantage that the synchrotron orbital radiation of a wide range wavelength area, for example, ultraviolet radiation and visible light, can be used.
[0014]
Namely, although the wavelength area of 200-400 nm and visible light is considered to be 400-800 nm, [the wavelength area of ultraviolet radiation] The photocatalyst in this invention method can use the synchrotron orbital radiation of a wavelength area as wide range as 250-500 nm, and can nitric-acid-ize nitrogen oxides unreacted more efficiently.
[0015]
As a light source made to generate artificially the synchrotron orbital radiation used in this invention method, an ultraviolet ray lamp, a xenon lamp, a fluorescent lamp, an incandescent lamp, etc. which are

commonly used, for example as a source of synchrotron orbital radiation can be mentioned.
[0016]
It is made to irradiate with synchrotron orbital radiation in this invention method, when performing the light response of nitrogen oxides continuously, contacting with oxygen the gas containing nitrogen oxides to a photocatalyst. Air can also be used instead of oxygen in this case.
[0017]
Although there is no restriction in particular about the oxygen concentration mixed in the gas in this case, since the nitric acid-ized efficiency of nitrogen oxides becomes high, it is so preferred that this concentration is large.
usually -- if oxygen to nitrogen oxides carries out comparatively -- per 1 mol of nitrogen oxides -- oxygen -- even if small, it is preferred to use 2 mol or more preferably 1 mol, but there is no restriction in particular.
Although nitric-acid-izing by the light response of nitrogen oxides requires existence of moisture, since meals can be enough provided by supply from a small amount of moisture adhering to a photocatalyst or a reaction vessel, or the component in the material which constitutes it, it is not necessary to add moisture in particular.
[0018]
[in this invention method] [the mixture of the gas and oxygen containing nitrogen oxides] [as a method of making a photocatalyst contacting] Both can be sealed hermetically in a well-closed container and all of a flow method to which the batch method and fluid in which a fluid and the photocatalyst surface are contacted by the thermal motion of a fluid are made to flow compulsorily, and a fluid and the photocatalyst surface are contacted can be used.
[0019]
Next, how to nitric-acid-ize nitrogen oxides by a light response, and detoxicate them using a photocatalyst, according to an accompanying drawing, is explained.
Drawing 1 is a longitudinal section showing one example of a suitable device to enforce this invention method, In the glass cylindrical well-closed container 1, the low pressure mercury lamp 3 made into the overcoat is arranged [photocatalyst / 2 /, i.e., the formless quartz glass pipe which carried out halide acid treatment,] in the surface, and these both ends have the end 4 of the well-closed container 1, and the structure supported by 4'.
[0020]
After flowing in the well-closed container 1 from the feed hopper 5, being mixed with the oxygen introduced from the oxygen feed port 6 and the gas containing nitrogen oxides contacting the photocatalyst 2, it is discharged from the outlet 7 outside. In the meantime, the mixture of nitrogen oxides and oxygen receives the exposure of the synchrotron orbital radiation from the low pressure mercury lamp 3, a light response is caused, and nitrogen oxides are nitric-acid-ized and disappear.
[0021]
After this device supplies the gas which contained nitrogen oxides and oxygen in the packed bed of silica provided with the window of quartz for an exposure of light, or quartz glass from the feed hopper 5 and contacts this packed bed and a fluid, it can also be made into the structure which may flow out of the outlet 7. As a feeding method of the gas in this device, although the method of forming a pressurization pump in the entrance side or the method of forming a decompression pump in an outlet side is common, the method of ventilating by a fan can also be used.
[0022]
Since a size of a packed bed and the rate of flow of gas are decided by concentration of nitrogen oxides to process and irradiation light intensity, processing unit structure, etc., a specific numerical value cannot prescribe. If it puts in another way, what is necessary will be for nitrogen oxides in gas to nitric-acid-ize by a light response, and just to set up an operating condition that the existence is hardly detected.
In this invention method, since nitrogen oxides disappear by a light response and nitric acid generates them, if this is washed in a succession process or it neutralizes with an alkali, nitrogen oxides leading to environmental pollution in gas are removable.
[0023]
As a light source in this device, when nitrogen oxides contact the photocatalyst surface, irradiation light intensity which may make this nitric-acid-ize can be generated, and there should just be no restriction in particular. As such a thing, sunlight irradiation equipment can be mentioned for usual ultraviolet ray lamp, xenon lamp, fluorescent lamp, and incandescent lamp as natural light equipment as artificial light equipment again.

[0024]
Drawing 2 is a longitudinal section showing one example of a device used when a batch method performs, Enclose gas which contains nitrogen oxides and oxygen from the gas inlet 9 provided with a valve into the well-closed container 1 provided with the window 8 for light irradiation (it isolates with the exterior with quartz or quartz glass) which inserted in the photocatalyst 2, and it lets the window 8 for light irradiation pass, Nitrogen oxides disappear, and after irradiating with synchrotron orbital radiation until nitric acid generates, gas containing nitric acid is taken out from the gas exhaust 10 provided with a valve. Nitrogen oxides can be removed easily, without performing excessive operation, if it does in this way. The above-mentioned window 8 for light irradiation can be made to form in arbitrary shape, such as planate, curved surface shape, and the shape of a cylinder.
[0025]
Since it can be produced by low cost since this device should just be a well-closed container which has a portion which has a window of quartz in which light irradiation is possible, or the product made from quartz glass, and holds a photocatalyst inside, and it can use sunlight, it can also make running cost low.
[0026]
As mentioned above, even if it uses which device, about the temperature which reacts, there is no restriction in particular and it can choose arbitrarily within the limits of -30 to 550 **. Although this light response advances enough under an atmospheric pressure, if it is a request, it can be pressurized and can also promote a reaction.
[0027]
[Working example]
Next, although an embodiment explains this invention still in detail, this invention is not limited at all by these.
The surface area of the photocatalyst in each example, the fill ration of the nitrogen oxides added into dry air, the light intensity of a light source, and a nitric acid yield are the numerical values measured by the following methods.
[0028]
(1) Surface area of a photocatalyst;
The surface area of the fused silica catalyst board measured the outer size method (length, width, thickness) with slide calipers, and calculated it as the sum of the area value of the 6th page of the outside from those values.
[0029]
(2) Fill ration of nitrogen oxides;
Gas containing nitrogen oxides were computed based on the nitrogen-oxides concentration and the amount of pressure variation which exist in introductory gas when it introduces into a reaction vessel.
[0030]
(3) Light intensity of a light source;
Using the detector only for measurement wavelength of an ultraviolet ray intensity meter (the Iuchi Seieido make, product name "UVR-400"), after light source lighting, after 30 minutes or more passed, the detector was installed in the catalyst fixed part in the central part of the reaction vessel, and the meter value was ****(ed) and calculated.
[0031]
(4) Nitric acid yield; the generation nitric acid gas concentration in a reaction vessel (320-ml capacity) was measured using the gas indicator tube (made by a gas tech company), and it computed as a rate to NO fill ration.
[0032]
In the embodiment, it was operated according to an order of following (a) thru/or (i) using the reactor shown in drawing 3.
[0033]
(a) Set sample pan SP who put the catalyst sample CS so that the sensor window W in the reaction vessel R might be coincided.
[0034]
(b) Drive vacuum pump P and open the method cock C1 of two, and C2. Three way stop cock CT2 is opened so that it may be in switch-on to a cock C 2-way. Three way stop cock CT3 is opened so that the cock C2 and the pressure sensing machine G may be in switch-on. And the gas (residual air) which exists between three way stop cock CT2 to three way stop cock CT3 and the pressure sensing machine G is exhausted.

[0035]
(c) When the directions value of the pressure sensing machine G is set to 1.0 or less Torr, close the cock C2.
[0036]
(d) Set massflow controller FC1 for oxygen gas supply as 20 ml/min, and set massflow controller FC2 for nitrogen gas supplying as 80 ml/min, make it drive and. The three way stop cocks CT3 and CT4 are made into switch-on so that those gas can be introduced to the reaction vessel R.
[0037]
(e) When the mixed gas of oxygen and nitrogen is supplied to the reaction vessel R via the mixed gas reservoir machine MR and the directions value of the pressure sensing machine G reaches atmospheric pressure power, intercept the three way stop cocks' CT3 and CT4 switch-on.
[0038]
The gas exchange (exhaust air and supply) operation in the reaction vessel R of (e) is repeated 3 times from (f) and (b). A vacuum pump will be suspended if the 4th exhaust air is completed. Next, three way stop cock CT3 is maintained at the switch-on of the reaction vessel R and the pressure sensing machine P, and NO reservoir machine NR and the cock C1 are made into switch-on for the three way stop cocks CT1 and CT2. NO gas is introduced into the reaction vessel R by this state. The initial fill ration of NO was computed from the variation and NO gas concentration of the pressure value (reading value of the pressure sensing machine P) in the reaction vessel R. If restoration of NO gas is completed, oxygen gas and nitrogen gas will be filled up into the reaction vessel R with operation of (d). When the pressure value (reading value of the pressure sensing machine P) in the reaction vessel R reaches atmospheric pressure power, the three way stop cocks' CT3 and CT4 switch-on is intercepted, and the method cocks C2 and C3 of two are closed. And the massflow controllers FC1 and FC2 are suspended.
[0039]
(g) Turn on the light source LS (example: low pressure mercury lamp), and apply the irradiation light LB to the catalyst sample CS through the window W for light-receiving.
[0040]
(i) The amount of generation nitric acid was measured after predetermined time light irradiation by letting the reactant gas in the reaction vessel R pass to a gas detector (made by a gas tech company) using a gas sampling machine.
In the inside E of a figure, a reactant gas extraction mouth is shown, and H shows the fringe of a reaction vessel, and the clasp of a lid.
[0041]
Reference example 1
It took out, after having accommodated 500 ml of hydrogen fluoride aqueous solutions of 10 mass % concentration in the container made from 1-l. volume polyethylene, immersing the fused silica sample of the kind shown in Table 1 into this in it and shaking for 12 minutes in 25 **, and it washed, and the photocatalyst was manufactured by drying. The total surface area of this photocatalyst is shown in Table 1.
[0042]
Reference example 2
After immersing the fused silica sample of the kind shown in Table 1 in the hydrogen fluoride aqueous solution of 5 mass % concentration and shaking for 10 minutes in 25 **, it washed and the photocatalyst was manufactured by drying. The total surface area of this photocatalyst is shown in Table 1.
[0043]
Embodiments 1-9, a comparative example
The light response of the dry air containing nitrogen monoxide of the quantity shown in Table 1 was performed using the photocatalyst and exposure conditions which are shown in Table 1. The result (nitric acid yield) is shown in Table 1.
[0044]
Embodiment 10
A light response of hydrous part air (moisture content 28micromol) containing nitrogen monoxide of quantity shown in Table 1 was performed using a photocatalyst and exposure conditions which are shown in Table 1. The result is shown in Table 1.
[0045]
[Table 1]

実施例	光触媒				NO充填量	放射光				硝酸生成率
	溶融石英の種類	形状	製造方法	表面積 (cm^2)	(μmol)	光源	波長範囲 (nm)	照射時間 (分)	光強度 (mW/cm^2)	(%)
1	GE214	半円筒板状	参考例1	50	3.57	低圧水銀灯	>230	120	0.15	3.6
2	GE214	半円筒板状	参考例2	50	3.60	低圧水銀灯	>230	120	0.15	4.1
3	GE219	半円筒板状	参考例1	57	3.64	低圧水銀灯	>230	120	0.15	2.9
4	GE219	半円筒板状	参考例1	50	3.57	低圧水銀灯	>230	120	0.15	1.8
5	GE214	半円筒板状	参考例1	60	3.57	自然光	—	120	—	1.7
6	GE214	半円筒板状	参考例1	140	3.56	ブラックライト	全光	120	0.79	4.1
7	GE219	半円筒板状	参考例1	57	3.66	蛍光灯	全光	120	FLE	1.8
8	GE254	半円筒板状	参考例1	50	3.57	蛍光灯	全光	120	FLE	1.7
9	GE214	半円筒板状	参考例1	60	3.57	低圧水銀灯	>230	60	0.15	1.2
10	GE214	半円筒板状	参考例1	140	2.10	低圧水銀灯	>230	60	0.15	5.5
対照	TiO_2	ガラス板コーティング	—	40	3.60	低圧水銀灯	>230	120	0.15	0

[0046]
FLE, a low pressure mercury lamp, and black lights are the following conditions.
(1)FLE;
Toshiba FL6M;6W
Visible optical power; 736 mW
Distance to the sample surface; 130 mm
(2) A low pressure mercury lamp;
The Seng light special light source; UVL-10
Light intensity on the surface of a sample; 0.15 mW/cm^2
;without ozone evolution wavelength > 230 nm
(3) A black light;
National FL6 BL-B;6W
Light intensity 0.19 mW/cm^2 on the surface of a sample
[0047]
According to this invention method, NO is nitric-acid-ized by operation of a photocatalyst, and this table shows decreasing. On the other hand, in the conventional TiO_2 photocatalyst, nitric acid-ization is hardly performed.
And since going via more advanced oxides, such as N_2O_3 and NO_2, and N_2O_5, is known in a process until it nitric-acid-izes this NO, If nitric acid-ization of NO is performed, it is clear that nitrogen oxides, such as N_2O_3, NO_2, and N_2O_5, can naturally also be nitric-acid-ized by this invention method.

[0048]
[Effect of the Invention]
According to this invention method, a new photocatalyst is used, and nitrogen oxides can be nitric-acid-ized, and can be decreased in number thru/or vanished.
[Brief Description of the Drawings]
[Drawing 1]The longitudinal section showing the example of a device for carrying out the light response of the nitrogen oxides continuously using this invention photocatalyst.
[Drawing 2]The longitudinal section showing the example of a device for carrying out the light response of the nitrogen oxides by a batch type using this invention photocatalyst.
[Drawing 3]The explanatory view of the reactor used in the embodiment.
[Explanations of letters or numerals]
1 Well-closed container
2 Photocatalyst
3 Light source
5 Fluid feed hopper
6 Oxygen feed port
7 Outlet
8 Window for light irradiation
9 Gas inlet
10 Gas exhaust
R Reaction vessel (with a cover)

W The window for light-receiving
CS Catalyst sample
SP Sample pan
P Vacuum pump
C1, C2, and C3 Method cock of two
CT1, CT2, CT3, CT4 three way stop cock
FC1 and FC2 Massflow controller
MR mixed gas reservoir machine
G Pressure sensing machine
NR NO reservoir machine
LS light source
LB Irradiation light
E Reactant gas extraction mouth
The fringe of H reaction vessel, and the clasp of a lid

[Translation done.]

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